

AD-A242 400

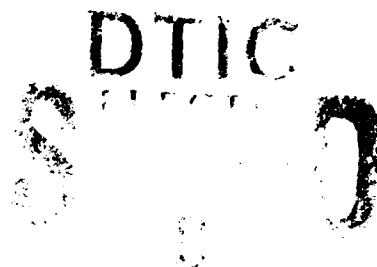


OFFICE OF NAVAL RESEARCH

Contract N00014-90-J-1828

R&D Code 413c024

Technical Report No. 54



Molecular Engineering of Liquid Crystal Polymers by Living
Polymerization. 17. Characterization of Poly{ 10-[(4-Cyano-4'-Biphenyl)
oxy]decanyl Vinyl Ether}s by 1-D and 2-D ^1H -NMR Spectroscopy

by

Virril Percec and Myongsoo Lee
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

and

Peter L. Rinaldi and Vincent E. Litman
Department of Chemistry
University of Akron
Akron, OH 44325

Accepted for Publication
in
J. Polym. Sci., Polym. Chem. Ed.

October 30, 1991

Reproduction in whole or in part is permitted for any purpose
of the United States Government.

This document has been approved for public release and sale.

Its distribution is unlimited.

91-15083



91 1105 002

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Available for distribution Distribution unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No.			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION Case Western Reserve University		6b OFFICE SYMBOL (If applicable) 4B566	7a NAME OF MONITORING ORGANIZATION ONR	
6c ADDRESS (City, State, and ZIP Code) 2040 Adelbert Road Cleveland, OH 44106			7b ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217	
8a NAME OF FUNDING/SPONSORING ORGANIZATION ONR		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 N. Quincy Arlington, VA 22217			10 SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO N00014-89	PROJECT NO J-1828
			TASK NO 413c024	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Characterization of Poly{10-[(4-Cyano-4'-Biphenyl)oxy]decanyl Vinyl Ether}s by 1-D and 2-D ¹ H-NMR Spectroscopy				
12. PERSONAL AUTHOR(S) Virgil Percec, Myongsoo Lee, Peter L. Rinaldi and Vincent E. Litman				
13a TYPE OF REPORT Preprint		13b TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) October 30, 1991	
15. PAGE COUNT				
16. SUPPLEMENTARY NOTATION J. Polym. Sci., Polym. Chem. Ed.				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>The characterization of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether}s obtained by living cationic polymerization initiated with CF₃SO₃H/S(CH₃)₂ in CH₂Cl₂ at 0°C and terminated by ammoniacal methanol, by 1-D and 2-D (COSY) 300 MHz ¹H-NMR spectroscopy is presented. The polymer contains one methyl and one methoxy chain ends, thus, demonstrating the absence of chain transfer and termination reactions. The number average degree of polymerization determined from the ¹H-NMR spectrum agree with the one expected from the [M]₀/[I]₀ ratio.</p>				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION unclassified/unlimited	
22a NAME OF RESPONSIBLE INDIVIDUAL Virgil Percec			22b TELEPHONE (Include Area Code) (216) 368-4242	22c. OFFICE SYMBOL

1. Question for
 2. the Board
 3. the fact
 4. the board
 5. the board
 6. the board
 7. the board
 8. the board
 9. the board
 10. the board
 11. the board
 12. the board
 13. the board
 14. the board
 15. the board
 16. the board
 17. the board
 18. the board
 19. the board
 20. the board
 21. the board
 22. the board
 23. the board
 24. the board
 25. the board
 26. the board
 27. the board
 28. the board
 29. the board
 30. the board
 31. the board
 32. the board
 33. the board
 34. the board
 35. the board
 36. the board
 37. the board
 38. the board
 39. the board
 40. the board
 41. the board
 42. the board
 43. the board
 44. the board
 45. the board
 46. the board
 47. the board
 48. the board
 49. the board
 50. the board
 51. the board
 52. the board
 53. the board
 54. the board
 55. the board
 56. the board
 57. the board
 58. the board
 59. the board
 60. the board
 61. the board
 62. the board
 63. the board
 64. the board
 65. the board
 66. the board
 67. the board
 68. the board
 69. the board
 70. the board
 71. the board
 72. the board
 73. the board
 74. the board
 75. the board
 76. the board
 77. the board
 78. the board
 79. the board
 80. the board
 81. the board
 82. the board
 83. the board
 84. the board
 85. the board
 86. the board
 87. the board
 88. the board
 89. the board
 90. the board
 91. the board
 92. the board
 93. the board
 94. the board
 95. the board
 96. the board
 97. the board
 98. the board
 99. the board
 100. the board
 101. the board
 102. the board
 103. the board
 104. the board
 105. the board
 106. the board
 107. the board
 108. the board
 109. the board
 110. the board
 111. the board
 112. the board
 113. the board
 114. the board
 115. the board
 116. the board
 117. the board
 118. the board
 119. the board
 120. the board
 121. the board
 122. the board
 123. the board
 124. the board
 125. the board
 126. the board
 127. the board
 128. the board
 129. the board
 130. the board
 131. the board
 132. the board
 133. the board
 134. the board
 135. the board
 136. the board
 137. the board
 138. the board
 139. the board
 140. the board
 141. the board
 142. the board
 143. the board
 144. the board
 145. the board
 146. the board
 147. the board
 148. the board
 149. the board
 150. the board
 151. the board
 152. the board
 153. the board
 154. the board
 155. the board
 156. the board
 157. the board
 158. the board
 159. the board
 160. the board
 161. the board
 162. the board
 163. the board
 164. the board
 165. the board
 166. the board
 167. the board
 168. the board
 169. the board
 170. the board
 171. the board
 172. the board
 173. the board
 174. the board
 175. the board
 176. the board
 177. the board
 178. the board
 179. the board
 180. the board
 181. the board
 182. the board
 183. the board
 184. the board
 185. the board
 186. the board
 187. the board
 188. the board
 189. the board
 190. the board
 191. the board
 192. the board
 193. the board
 194. the board
 195. the board
 196. the board
 197. the board
 198. the board
 199. the board
 200. the board
 201. the board
 202. the board
 203. the board
 204. the board
 205. the board
 206. the board
 207. the board
 208. the board
 209. the board
 210. the board
 211. the board
 212. the board
 213. the board
 214. the board
 215. the board
 216. the board
 217. the board
 218. the board
 219. the board
 220. the board
 221. the board
 222. the board
 223. the board
 224. the board
 225. the board
 226. the board
 227. the board
 228. the board
 229. the board
 230. the board
 231. the board
 232. the board
 233. the board
 234. the board
 235. the board
 236. the board
 237. the board
 238. the board
 239. the board
 240. the board
 241. the board
 242. the board
 243. the board
 244. the board
 245. the board
 246. the board
 247. the board

SUMMARY

The characterization of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} obtained by living cationic polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 at 0°C and terminated by ammoniacal methanol, by 1-D and 2-D (COSY) 300 MHz ^1H -NMR spectroscopy is presented. The polymer contains one methyl and one methoxy chain ends, thus, demonstrating the absence of chain transfer and termination reactions. The number average degree of polymerization determined from the ^1H -NMR spectrum agrees with the one expected from the $[\text{M}]_0/[\text{I}]_0$ ratio.

Keywords: living cationic, chain ends, 2-D ^1H -NMR spectroscopy.

INTRODUCTION

Since the first examples of mesogenic vinyl ethers and liquid crystalline poly(vinyl ether)s were reported from our laboratory (1), several research groups became actively engaged in the synthesis of liquid crystalline poly(vinyl ether)s mainly because they can be polymerized by living cationic mechanism (2,3,4). So far, we have elucidated the influence of molecular weight on the phase transitions of poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s with alkyl groups from ethyl to undecanyl (5). Binary copolymerization experiments performed with the same monomers at constant copolymer molecular weight allowed the molecular design of nematic, smectic A and reentrant nematic mesophases (6). Similar homopolymerization and copolymerization experiments were used to tailor make polymers exhibiting a chiral smectic C mesophase (7). In addition, it has been shown that many functional mesogenic vinyl ethers (8) can be polymerized by our preferred initiating system $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 (9).

The experiments described so far (5-8) required only a good control over the degree of polymerization and polydispersity of the polymer. In order to synthesize more complex architectures derived from liquid crystalline poly(vinyl ether)s we have to control in a quantitative manner the nature of the polymer chain ends. This has been shown to be possible with polymers derived from alkyl vinyl ethers (10). The simplest avenue available to check the capability to functionalize the chain ends of poly{ ω -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s is by providing a quantitative analysis of the polymer obtained after termination with ammoniacal methanol. This communication describes the characterization of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} by 1-D and 2-D 300 MHz ^1H -NMR spectroscopy.

EXPERIMENTAL

The synthesis of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} (6-10), its living cationic polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in CH_2Cl_2 at 0°C and the characterization of the resulted polymers were presented in a previous publication from our laboratory (5d).

The 1-D ^1H and 2-D ^1H -NMR (COSY) spectra were recorded at 299.55 MHz on a VXR-300 NMR spectrometer equipped with a 5 mm indirect detection probe in CDCl_3 at room temperature. 1-D spectra were obtained with a 5,600 Hz spectral width, 2.926 s acquisition time, 4 μs 130° pulse, 0 s relaxation delay and 2,048 transients. The

2-D ^1H -NMR (COSY) spectra were obtained with a 2,775.5 spectral width, 0.184 s acquisition time, 13 μs 90° pulse, 1 s delay between transients and 32 transients.

RESULTS AND DISCUSSION

Poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} (6-10) with a theoretical degree of polymerization of four and $M_w/M_n=1.15$ was synthesized by initiation with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ in methylene chloride at 0°C . The polymerization was terminated by methanol containing ammonia. Details of this polymerization were presented previously (5d). The ideal structure of poly(6-10) resulted from this living polymerization reaction is shown in Scheme 1. Scheme 2 outlines the structure of the chain ends expected to result from the chain transfer to monomer and counter anion and from termination reactions.

Figure 1 shows the 1-D ^1H -NMR spectrum of poly(6-10) together with its proton assignments. 2-D ^1H -NMR spectrum is presented in Figure 2. The aromatic region of the poly(6-10) is presented in Figure 2a while the aliphatic part of the same spectrum in Figure 2b. The off-diagonal cross-peaks from Figure 2a,b indicate which protons are J-coupled and support the assignment of proton resonances from Figure 1. The chemical shifts of these assignments are summarized in Table 1. The signals due to the methyl (signal a), methoxy (signal f) and acetal $-\text{CH}_2(\text{O})\text{CHO}-$ (signal e), chain ends were integrated. Their experimental ratios (i.e., $f/a=1$ and $a/e\approx 3.0$) correspond to the theoretical values expected for a polymer resulted from a polymerization free of chain transfer and termination reactions (Table II). The calculated degree of polymerization ($\text{DP}=n/2e=3.4$) is very close to the theoretical one i.e., $[\text{M}]_0/[\text{I}]_0=4.0$.

In addition, the NMR spectra of this polymer do not show any unsaturated chain ends which would result from chain transfer reactions. Only a very small signal at 9.8 ppm can be observed. This signal is due to a $-\text{CHO}$ chain end which results from the termination reaction. However, it represents less than 1% of the total concentration of the methoxy chain end. The ^1H -NMR spectra of poly(6-10)s with degree of polymerization up to 30 were analyzed and show the same behavior. These results demonstrate that a quantitative functionalization of the poly(6-10) prepared with this initiation system is possible and that the absolute number average molecular weight of the polymers with degrees of polymerization up to 30 can be determined by ^1H -NMR spectroscopy (7).

ACKNOWLEDGMENTS

Financial support from the Office of Naval Research is gratefully acknowledged.

REFERENCES AND NOTES

1. J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci.; Part A; Polym. Chem.*, **29**, 327(1986); V. Percec and D. Tomazos, *Polym. Bull.*, **18**, 239(1987)
2. (a) T. Sagane and R. W. Lenz, *Polym. J.*, **20**, 923(1988); (b) T. Sagane and R. W. Lenz, *Polymer*, **30**, 2269(1989); (c) T. Sagane and R. W. Lenz, *Macromolecules*, **22**, 3763(1989).
3. S. G. Kostromin, N. D. Cuong, E. S. Garina and V. P. Shibaev, *Mol. Cryst. Liq. Cryst.*, **193**, 177(1990)
4. V. Heroguez, A. Deffieux and M. Fontanille, *Makromol. Chem., Makromol. Symp.*, **32**, 199(1990); V. Heroguez, M. Schappacher, E. Papon and A. Deffieux, *Polym. Bull.*, **25**, 307(1991).
5. (a) V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci.: Part A: Polym. Chem.*, **29**, 327(1991); (b) V. Percec and M. Lee, *J. Macromol. Sci.-Chem.*, **A 28**, 651(1991); (c) V. Percec and M. Lee, *Macromolecules*, **24**, 1017(1991); (d) V. Percec and M. Lee, *Macromolecules*, **24**, 2780(1991); (e) V. Percec, M. Lee and C. Ackerman, *Polymer*, in press.
6. V. Percec and M. Lee, *Polym. Bull.*, **25**, 123(1991); V. Percec and M. Lee, *Polym. Bull.*, **25**, 131(1991); V. Percec and M. Lee, *Macromolecules*, **24**, 4963(1991); V. Percec and M. Lee, *Polymer*, in press; V. Percec and M. Lee, *J. Mater. Chem.*, in press.
7. V. Percec, Q. Zheng and M. Lee, *J. Mater. Chem.*, **1**, 611(1991); V. Percec, Q. Zheng and M. Lee, *J. Mater. Chem.*, in press
8. R. Rodenhouse, V. Percec and A. E. Feiring, *J. Polym. Sci.: Part C: Polym. Lett.*, **28**, 345(1990); H. Jonsson, V. Percec and A. Hult, *Polym. Bull.*, **25**, 115(1991); R. Rodenhouse and V. Percec, *Adv. Mater.*, **3**, 101(1991); V. Percec, A. E. Gomez and M. Lee, *J. Polym. Sci.: Part A: Polym. Chem.*, in press; V. Percec, C. S. Wang and M. Lee, *Polym. Bull.*, **26**, 15(1991)
9. C. G. Cho, B. A. Feit and O. W. Webster, *Macromolecules*, **23**, 1918(1990); C. H. Lin and K. Matyjaszewsky, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **31**(1), 599(1990).

10. For recent reviews on living cationic polymerization of olefines see: M. Sawamoto, *Progr. Polym. Sci.*, **16**, 111(1991); M. Sawamoto and T. Higashimura, *Makromol. Chem., Makromol. Symp.*, in press; For some recent publications on chain ended functional poly(vinyl ether)s see: S. Chakrapani, R. Jerome and Ph. Teyssie, *Macromolecules*, **23**, 3026(1990); M. Schappacher and A. Deffieux, *Macromolecules*, **24**, 2140(1991); E. J. Goethals, N. H. Haucourt, A. M. Verheyen and J. Habimana, *Makromol. Chem., Rapid Commun.*, **11**, 623(1990).

FIGURES AND SCHEME CAPTIONS

Figure 1: 300 MHz 1-D ^1H -NMR spectrum of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} with theoretical degree of polymerization of 4.

Figure 2: 2-D ^1H -NMR (COSY) spectrum of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} with theoretical degree of polymerization of 4: a) aromatic region; b) aliphatic region.

Scheme 1: The ideal structure of poly{10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether} obtained by living polymerization initiated with $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ and terminated with ammoniacal methanol.

Scheme 2: Chain transfer and termination reactions.

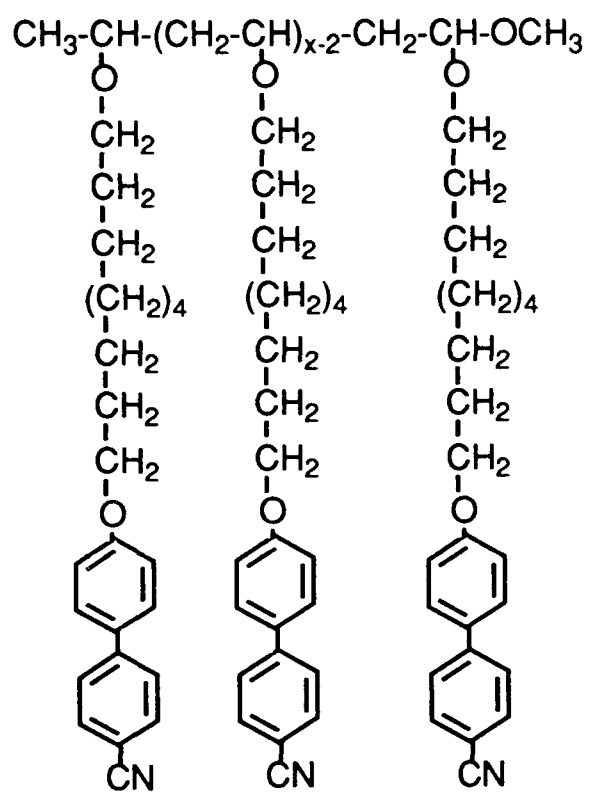
Table I. ^1H -NMR Chemical Shifts of Poly(6-10)

proton	label	chemical shift (ppm)	nature of signal
polymer backbone	a	1.12	d
	b	3.50	m
	c	1.75	m
	d	1.75	m
	e	4.60	m
	f	3.30	s
flexible spacer	g	3.43	m
	h	1.53	m
	i	1.42	m
	j	1.29	m
	k	1.44	m
	l	1.78	m
	m	3.90	t
aromatic region	n	6.94	d
	o	7.47	d
	p	7.65	d of d
	q	7.65	d of d

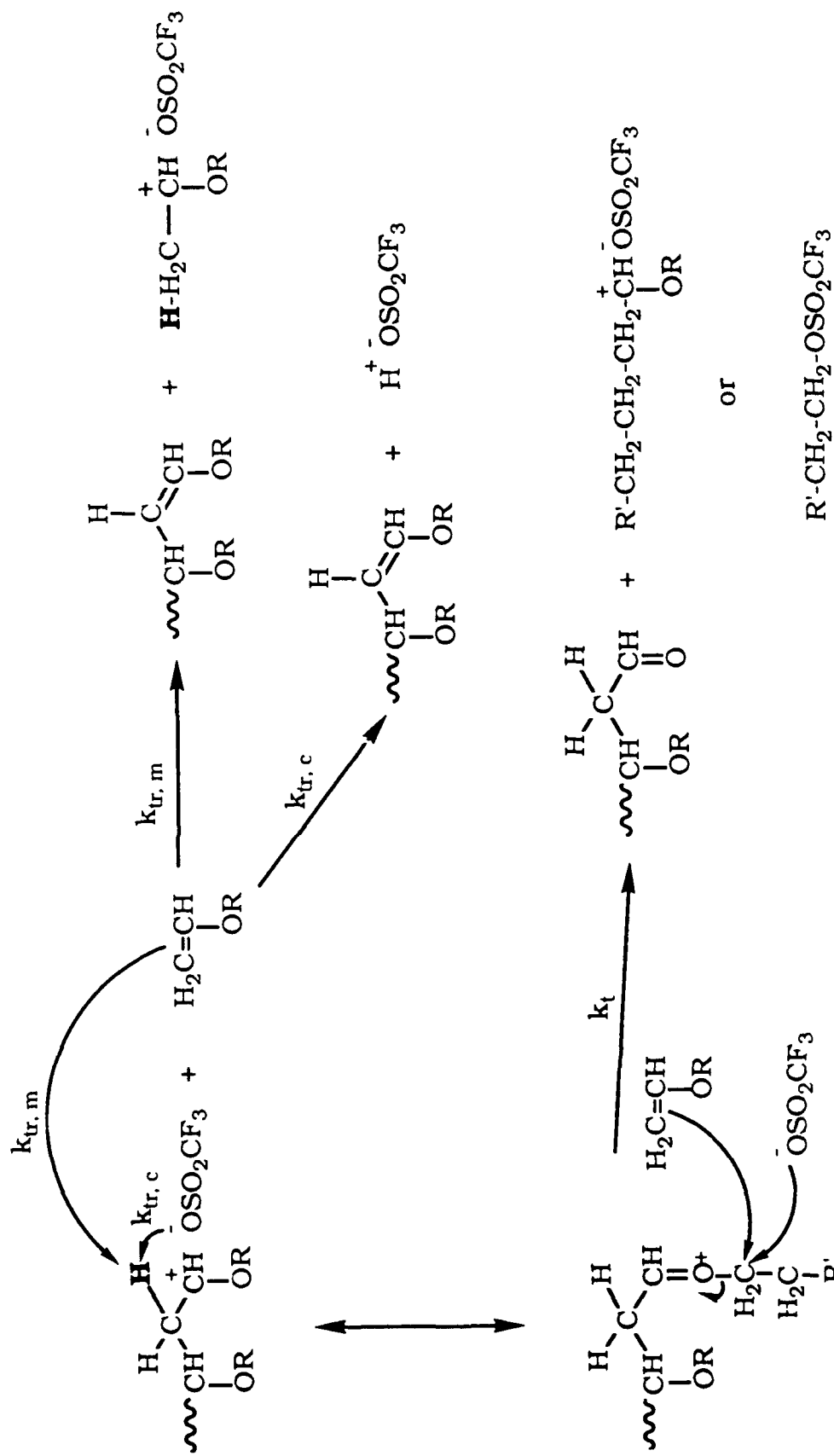
Table II. Integration Ratio of Polymer Chain Ends

proton	integration ratio (NMR)	theoretical ratio
f/a	0.96 ^a	1.0
n/e	6.80 ^b	8.0
a/e	2.87	3.0

^a Number of methoxy end groups/polymer chain^b DP (NMR)=6.8/2=3.4



Scheme 1



Scheme 2

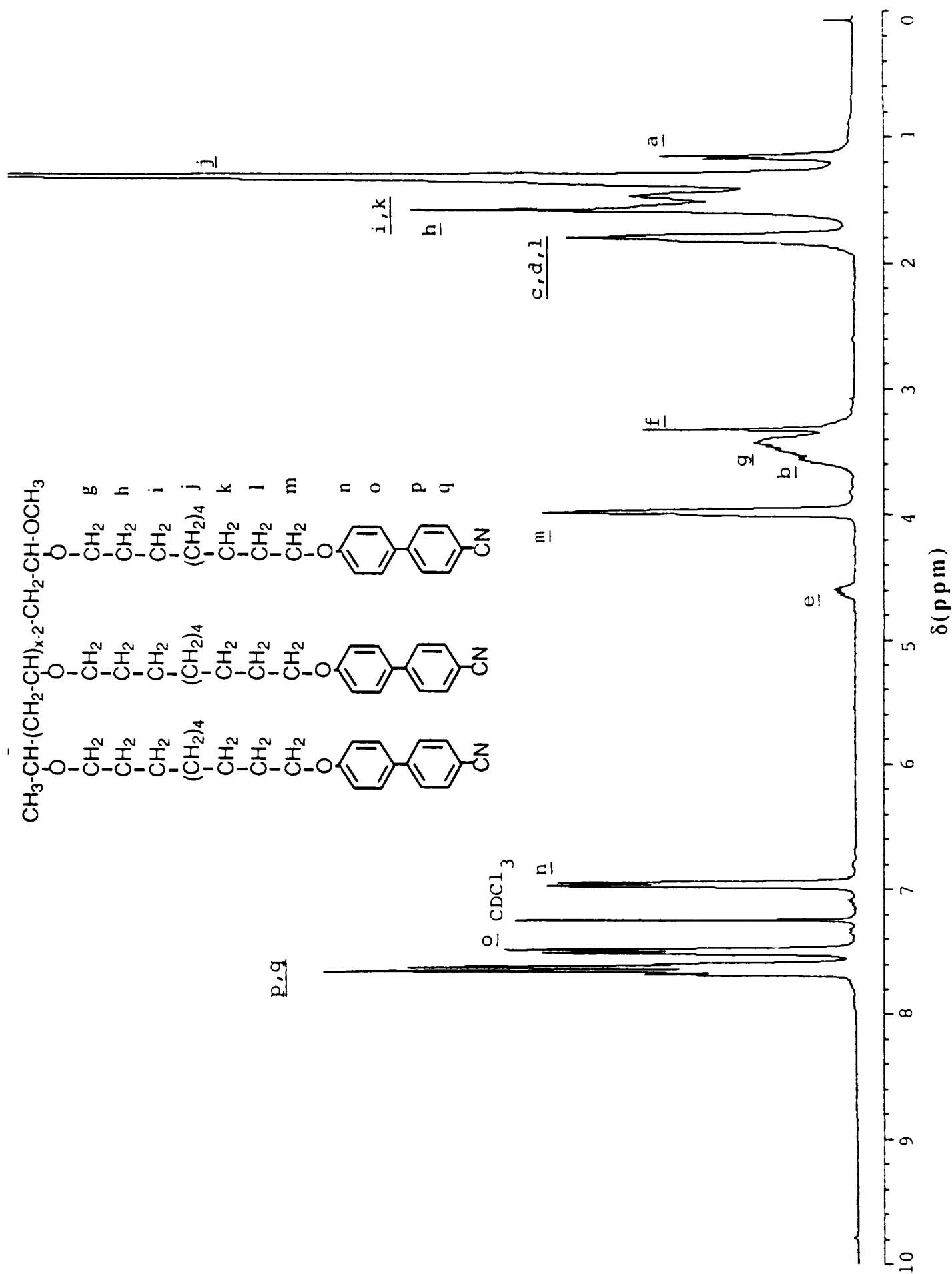


Figure 1

Figure 2a

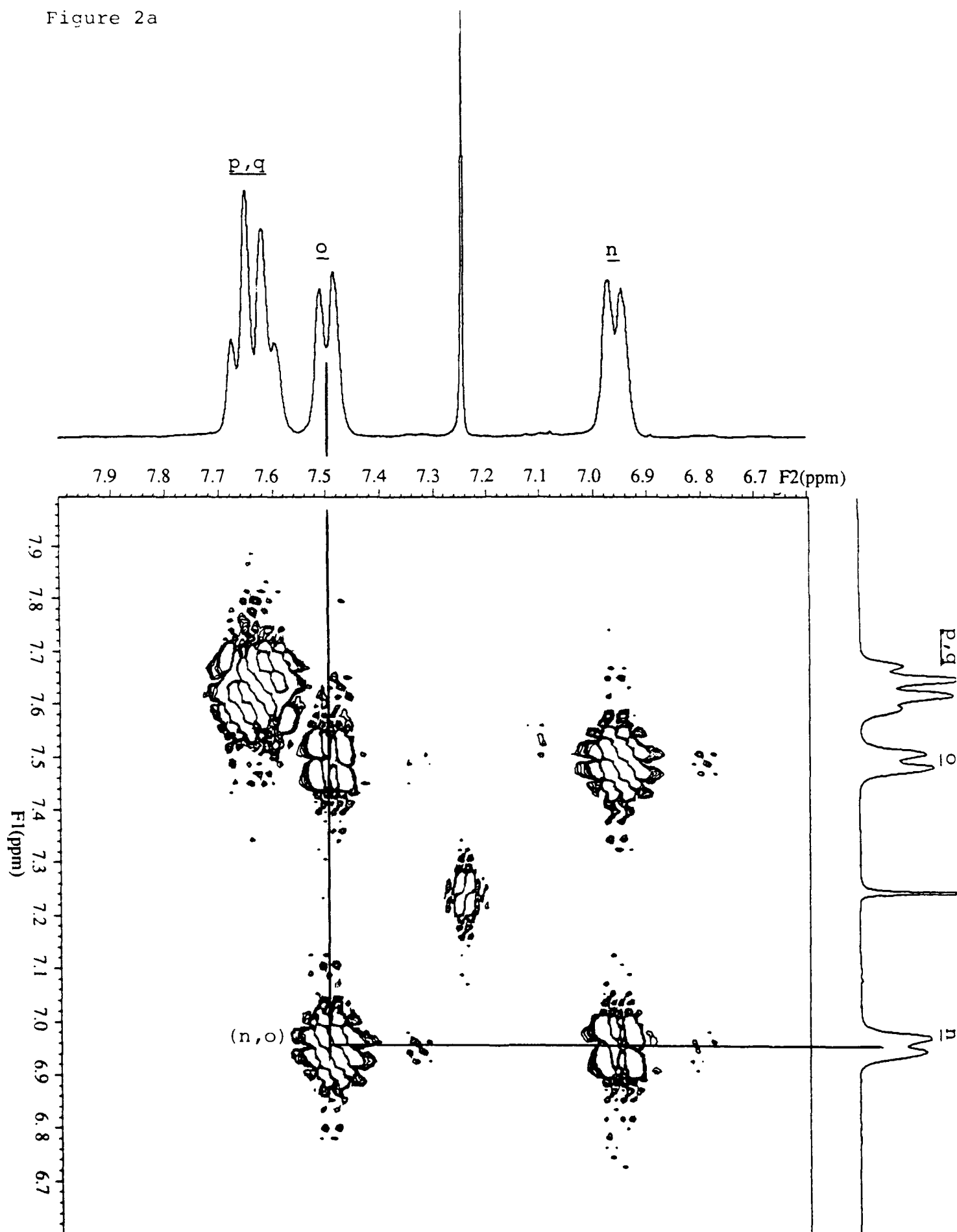


Figure 2b

